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Dated 17 December 1998

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P01/7700 25.00 - 9805407.5

The Patent Office

Cardiff Road
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1. Your reference

PB751/II/GB/RGMS

2. Patent application
(The Patent Office)

9805407.5

14 MAR 1998

3. Full name, address and postcode of the or of each applicant (underline all surnames)

ALBRIGHT & WILSON UK LIMITED
210-222 HAGLEY ROAD WEST
OLDBURY
WEST MIDLANDS B68 0NN

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND

6804264001

4. Title of the invention

BIOCIDAL COMPOSITIONS AND TREATMENTS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

R G M SAVIDGE
ALBRIGHT & WILSON UK LIMITED
PATENTS DEPARTMENT
PO BOX 3
210-222 HAGLEY ROAD WEST
OLDBURY
WEST MIDLANDS
B68 0NN

Patents ADP number (if you know it)

5249004

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

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Continuation sheets of this form	NONE
Description	6 PAGES
Claim(s)	NONE
Abstract	NONE
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10. If you are also filing any of the following, state how many against each item.

Priority documents	NONE
Translations of priority documents	NONE
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	NONE
Request for preliminary examination and search (Patents Form 9/77)	NONE
Request for substantive examination (Patents Form 10/77)	NONE
Any other documents (please specify)	NONE

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date 13 March 1998

R G M SAVIDGE - By Power of Attorney

12. Name and daytime telephone number of person to contact in the United Kingdom

MR R G M SAVIDGE
0121 420 5430

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PB751/II

PATENTS ACT 1977

PRELIMINARY SPECIFICATION
(Description)

BIOCIDAL COMPOSTIONS AND TREATMENTS

Applicant : **ALBRIGHT & WILSON UK LIMITED**

Inventors :



PB751/II/GB

BIOCIDAL COMPOSITIONS AND TREATMENTS

The present invention relates to synergistic biocidal mixtures of hydroxymethyl phosphonium biocides with polymers and copolymers of quaternary ammonium salts.

GB 2 145 708 describes biocidal uses of tetrakis (hydroxymethyl) phosphonium salts, referred to herein collectively as "THP". US 4 778 813 describes the biocidal use of quaternary ammonium polymers. GB 2 178 960 describes synergism between THP and surfactant. GB 2 228 680 describes synergism between THP and certain aldehydes.

THP formulations are increasingly widely used as biocides for water treatment in treating cooling water, process water e.g. in pulp and paper manufacture, drilling fluids and other aerobic water systems, as well as in anaerobic systems such as oil field formation water, injection water, produced water and water used in hydrostatic testing. Advantages include rapid and effective bactericidal activity and environmental acceptability. Particularly in systems where slime forming bacteria proliferate (e.g. in aerobic systems such as cooling water) it has been found desirable to use THP formulations containing synergistic amounts of a surfactant according to GB 2 178 960, in order to improve cost effective biocidal action. However such formulations cause foaming problems. Attempts to combine THP with other biocides (e.g. aldehydes), which do not cause foaming, have not been able to provide such effective biocidal action against slime forming bacteria, and/or have detracted from the favourable environmental profile of THP.

We have now discovered that combinations of THP with quaternary ammonium polymers and copolymers provide strongly synergistic biocidal formulations which give excellent penetration of bacterial slime and improved activity against planktonic bacteria without causing excessive foam.

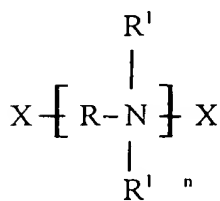
Our invention provides a biocidally synergistic mixture comprising THP and at least one quaternary ammonium polymer or copolymer.

According to a second embodiment the invention provides a method of treating aqueous systems contaminated, or liable to contamination, with bacteria, fungi or algae which comprises applying thereto separately or together a biocidally active amount of the components of a synergistic mixture as aforesaid.

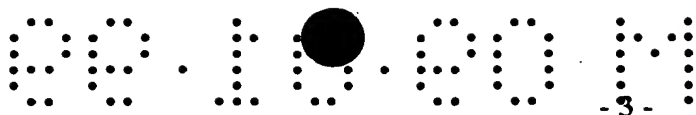
The aqueous system may, for instance, be contaminated with bacterial slime. The invention is of use for treating aerobic systems and also for anaerobic systems.

The THP salt is preferably the sulphate, chloride or phosphate. However any water soluble salt may be used including the nitrate, phosphite, bromide, fluoride, carbonate, acetate, formate, citrate, borate, or silicate. In fact any counter ion which is chemically compatible with the THP cation may be used, the main criteria for selection being economic.

The quaternary ammonium polymer may be any of those described in US 4 778 813. Particularly preferred is poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride]. This is a copolymer of NNN¹N¹-tetramethyl-1,2-diamino ethane with bis (2-chloroethyl) ether, which is referred to herein as "WSCP". The latter is the commercial name of the product used in the example, which is sold by Buckman Laboratories. However any other water soluble polymer containing a plurality of quaternary ammonium groups may be used. Such compounds typically have the formula:



wherein each R is a divalent organic group constituting with the ammonium group a monomeric residue or separately selected from two or more comonomeric residues each R¹ is an alkyl or hydroxy alkyl group, preferably methyl or ethyl, X is hydrogen or a



monovalent inorganic or organic end capping group and n is from 3 to 3000, e.g. 5 to 2000, especially 8 to 1000, e.g. 10 to 500, most preferably 20 to 100.

Some typical examples include:

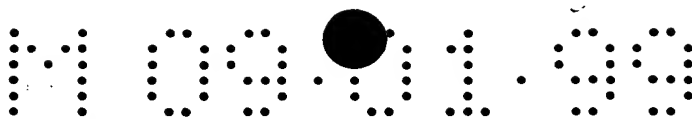
Poly[hydroxyethylene(dimethyliminio)ethylene(dimethyliminio)methylene dichloride]

Poly[hydroxyethylene(dimethyliminio)-2-hydroxypropylene(dimethyliminio)-methylene dichloride]

[*N*-[3-(dimethylammonio)propyl]-*N'*[3-(ethyleneoxyethylenedimethylammonio)propyl]urea dichloride]

α -4-[1-tris(2-hydroxyethyl)ammonium chloride-2-butenyl]poly[1-dimethylammonium chloride-2-butenyl]- ω -tris(2-hydroxyethyl)ammonium chloride

The relative weight proportions of the THP and the polymer may range from 1:1000 to 1000:1, preferably 1:200 to 500:1, more preferably 1:100 to 200:1, most preferably 1:50 to 100:1, especially 1:10 to 50:1, more usually 1:5 to 20:1, e.g. 1:1 to 10:1.



The invention will be illustrated by the following examples:-

Example 1

THPS/WSCP mixture was compared with two commercial THP/anionic surfactant products for control of legionella pneumophila.

METHODOLOGY

Parameter	Details
Test medium	Sterile WHO Standard hardness water (total hardness 342mg litre ⁻¹) plus 3mg litre ⁻¹ iron as ferric sulphate
Biocides	Stock solutions 10 x the concentration to be tested are prepared in WHO standard hardness water
pH	8.0 0.2
pH adjuster	Boric acid/borax buffer as contained in the test medium
Test organism	<i>L pneumophila</i> sg 1 (NCTC 11192)
Test volume	10ml
Contact temp	21 ± 1°C
Contact times	0, 3, 4 and 6 hours
Inoculum level	To give an initial concentration of approximately 1 x 10 ⁵ cfu/litre
Preparation of inoculum	Resuscitate test organism from lyophilised culture. Prepare 48h plate culture on BCYE agar. Hold at 4°C overnight. Suspend in 10ml of test medium.
Test method	Add 1ml of biocide stock solution to 8ml of test medium. Control contains 9ml of test medium only. At time 0h add 1ml of inoculum. After the appropriate contact times remove 1ml and make serial 10 x dilutions.
Enumeration method	By performing Miles and Misra dilution counts onto BCYE agar plates.
Replication	Spot 33 microlitres of each dilution in triplicate onto dry BCYE agar plates to obtain a mean count of surviving legionellae.
Plate incubation temperature	37 ± 1°C
Plate incubation period	7 days
Expression of results	Give number of control and surviving legionellae and the log 10 reduction in numbers of biocide-treated cell suspensions compare to the appropriate controls.

RESULTS

The results are summarised below

Product	3 Hour Contact Time			4 Hour Contact Time			6 Hour Contact Time		
	25ppm	50ppm	100ppm	25ppm	50ppm	100ppm	25ppm	50ppm	100ppm
34% THP 2% anionic surfactant (Comparison A)	1×10^3	6×10^2	1.6×10^3	1.5×10^2	15	ND	30	ND	ND
74% THP 1% anionic surfactant (Comparison B)	6×10^4	4.5×10^2	ND	1.4×10^4	6×10^2	ND	4.5×10^2	ND	ND
50% active THP / 0.7% WSCP (Example)	3×10^3	ND	ND	5.3×10^2	ND	ND	30	ND	ND

- Notes: i) ND - Non Detected
- ii) The control was 1×10^5
- iii) The following conclusions apply:-
- > A - Good activity within 4 hours at 50ppm or above
 - > B - Good activity within 3 hours at 100 ppm or 6 hours at 50ppm
 - > Example - Good activity within 3 hours at 50 ppm or above

The example of the invention also showed superior performance to conventional THP surfactant formulations, to WSCP alone and to THP alone in reducing planktonic bacteria.

The example gave less than half the foaming observed using surfactant containing formulations.

Example 2

An aqueous solution comprising 50% THPS and 2% WSCP was added to alginate beads infected with sulphate reducing bacteria. When dosed at 250ppm, the solution gave a 100 fold reduction in bacterial counts, compared with a control, after two weeks incubation.

At 500ppm the solution gave a total kill.

The mixture also gives effective control over fungi and algae.

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